

IN THE SPECIFICATION:

Please replace paragraph [0008] with the following amended paragraph:

[0008] Embodiments of the invention further provide a method for replenishing a copper plating solution. The method includes receiving a portion of a used copper plating solution in a first end of a depletion chamber or dilute cell of an electrodialysis cell, and urging positively charged copper and H⁺ ions into a concentration chamber or brine cell, while also urging negatively charged sulfate ions into the concentration chamber. The method further includes generating concentrated copper sulfate/sulfuric acid solution in the concentration chamber, and returning the concentrated copper sulfate/sulfuric acid solution to the copper plating solution.

Please replace paragraph [0018] with the following amended paragraph:

[0018] Figure 2 illustrates a schematic view of an exemplary EDC cell 103 of the present invention. The exemplary EDC cell 103, for example, may be implemented into an ECP system configured to plate copper onto semiconductor substrates. The exemplary EDC cell 103 generally includes an outer housing 201 configured to hold or confine the essential elements of EDC 103. A first end of housing 201 generally includes an anode source 203, while a second end of housing 201 generally includes a cathode source 202. Anode source 203 and cathode source 202 are generally positioned on opposite/opposing ends of housing 201. The volume between cathode source 202 and anode source 203 within housing 201 generally includes a plurality of EDC chambers, wherein the EDC chambers generally include alternating concentration chambers 204 and electrolyte depleting chambers 205. For example, as illustrated in Figure 2, an alternating series of depleting chambers 205 and concentration chambers 204 are positioned between the anode source 203 and the cathode source 202 within housing 201. Additionally, the first and second ends of cell 203 may include an anode chamber 207 211 and a cathode chamber 206 212 corresponding to the anode 207 or

cathode 206 positioned in the respective end of housing 201, wherein these chambers separate the respective anode and cathode from the input depletion 205 and concentration 204 chambers. The respective chambers 204, 205 are individually separated by selectively permeable membranes 209, 210.

Please replace paragraph [0020] with the following amended paragraph:

[0020] The respective chambers 204,205 are individually separated by anionic membranes 209 and cationic membranes 210. The particular configuration of anionic membranes 209 and cationic membranes 210 illustrated in Figure 2 operates to generate alternating concentration chambers 204 and depleting chambers 205. Although four depletion chambers 205 and three concentration chambers 204 are illustrated in the embodiment of Figure 2, the present invention contemplates generally any number of concentration and depletion chambers may be used. For example, embodiments of the invention contemplate that the total number of concentration chambers may be between about 5 and about 500, for example. Additionally, EDC 103 includes a cathode chamber 212 and an anode chamber 211 positioned immediate the respective cathode 202 206 and anode electrodes 203 207. Cathode and anode chambers 212 and 211 may be supplied with a sulfuric acid solution via conduit 214, which may operate to circulate the acid solution through the respective chambers.

Please replace paragraph [0021] with the following amended paragraph:

[0021] In operation, used electrolyte from a plating system is delivered to depletion chambers 205 via conduit 208, while an electrical bias is applied across EDC cell 103 via anode 203 207 and cathode 202 206. The electrical bias generated by anode 203 207 and cathode 202 206 urges positive copper ions and hydrogen ions in the used electrolyte solution towards the cathode 202 206, while simultaneously urging negatively charged sulfate ions in the used electrolyte solution towards the anode 203 207. Further, the configuration of anionic membranes 209 and cationic membranes 210 operate to capture the positive copper and H⁺ ions and the negative sulfate ions in the

concentration chambers 204, where these ions may combine to form copper sulfate and sulfuric acid. The formed acidic copper sulfate solution may then be removed from concentration chambers 204 via fluid outlet 215 and be re-circulated into the plating system (or an electrolyte solution tank, etc.), as CuSO₄/H₂SO₄ CuSO₄/H₂SO₄ are primary elements of an electrolyte solution for a copper electroplating system. Further, the configuration of anionic membranes 209 and cationic membranes 210 operates to confine the contaminants in the used electrolyte solution deposited into depletion chambers 205 therein. As such, the contaminants that are confined within depletion chambers 205, which generally comprise depleted and decomposed organics, small solid particles and traces of acid and copper, may be removed therefrom via fluid outlet 213 and disposed of or neutralized, as desired. Therefore, EDC 103 generally operates to receive used electrolyte from a plating system and separate viable components (copper sulfate and sulfuric acid) from the used electrolyte for reuse in the plating system.

Please replace paragraph [0022] with the following amended paragraph:

[0022] Figure 3 shows a more detailed illustration of the operation of EDC cell 103. In this embodiment, aged electrolyte is supplied to EDC cell 103 via conduit 208, which may ~~be includes~~ include communication with and an electrolyte drain of an ECP cell. Conduit 208 supplies the aged electrolyte into a plurality of depletion cells or chambers 205 in the EDC cell 103. While the aged electrolyte is being supplied to the depletion ~~cells~~ cells 205, an electrical bias is applied across EDC cell 103 via cathode 202 206 and anode 203 207. In the illustrated EDC cell 103 configuration, the electrical bias supplied thereto may be about 7 volts, for example, however, the electrical bias may be increased or decreased in order to adjust the process parameters. However, generally, the bias applied across the EDC cell 103 for the purpose of extracting contaminants from a plating solution made generally be calculated as a ballot one volt of electrical bias for each cell/chamber within EDC cell 103. Therefore, inasmuch as there are 7 cells/chambers within EDC cell 103 (3 concentration chambers and 4 depletion

chambers), the electrical bias supplied between cathode 202 206 and anode 203 207 may be approximately 7 volts.

Please replace paragraph [0023] with the following amended paragraph:

[0023] The application of the electrical bias across EDC cell 103 operates to urge ions in the aged electrolyte solution towards the respective poles, i.e., positive ions will be urged in the direction of the cathode, while negative ions will be urged in the direction of the anode. Therefore, the disassociated copper ions in the aged electrolyte solution, which are generally illustrated as Cu^{2+} in Figure 3, along with positive hydrogen ions (H^+), are urged in the direction of cathode 202 206. Similarly, disassociated sulfate ions in the aged electrolyte solution, which are generally illustrated as SO_4^{2-} , are urged in the direction of anode 203 207. However, although the respective ions are urged in the direction of the respective poles, the linear distance the respective ions are allowed to travel is limited by the positioning of the anionic and cationic membranes 209,210. More particularly, the positive copper and hydrogen ions in depletion cells 205 are urged towards cathode 202 206, and are allowed to pass into the neighboring concentration chamber 204, as the membranes separating deletion chamber 205 and concentration chamber 204 is a cationic membrane 210, which may generally be configured to transmit the respective positive ions therethrough in the direction of the cathode 202 206. Similarly, the negatively charged sulfate ions are urged towards the anode 203 207 and are allowed to pass into the neighboring concentration chamber 204 by an anionic membrane 209, which made generally be configured to transmit negative ions therethrough in the direction of the anode 203 207. As a result of the alternating positioning of the cationic and anionic membranes 210,209, positive copper ions and negative sulfate ions are allowed to diffuse into concentration chambers 204, where these ions may combine to form concentrated copper sulfate-sulfuric acid solution ($CuSO_4/H_2SO_4$ H_2SO_4). This concentrated copper sulfate may then be removed from concentration chambers 204 via outlet 215 and returned to the plating system, as concentrated acidic copper sulfate solutions all are a common component in copper ECP baths.

Please replace paragraph [0024] with the following amended paragraph:

[0024] The hydrogen ions behave similarly to Cu ions, in that when the hydrogen ions enter concentration chambers 204 they form H₂SO₄ upon combining with the SO₄²⁻ ions. Thus, in embodiments of the invention, a goal is to transfer CuSO₄ and H₂SO₄ from the depletion chambers 205 to concentration chambers 204, while the solution contaminants (organic contaminants, impurities, breakdown chains, solid particles, etc.) remain in depletion chambers 205. The difficulty in this process is generally maintaining a CuSO₄/H₂SO₄ CuSO₄/H₂SO₄ solution in the concentration chambers 204, where the concentration of Cu and acid is at least the same as an initial contaminated solution (or in the plating bath). This process is difficult, as the H⁺ ions migrate and diffuse through the membranes approximately 100 times faster than the Cu ions. Additionally, anionic membranes are generally partially permeable for the H⁺ ions as they migrate towards the cathode, which is generally termed "back migration" or "high diffusivity of H⁺" effect. To decrease the negative influence of H⁺ ions, embodiments of the present invention utilize anionic membranes having a dense population of canals. The size of canals is generally between about 1 and about 10 nm. For example, Neosepta membranes, ACS membranes, and AM3 membranes have these properties. Additionally, the selectivity of anion membranes increases (or H⁺ back migration decreases) in diluted solutions. Therefore, in order to improve the anionic membrane transport properties and to prevent penetration of H⁺ through anionic membrane, the present invention implements intermediate chambers with diluted H₂SO₄ between depletion and concentrate chambers.

Please replace paragraph [0026] with the following amended paragraph:

[0026] The outermost chambers of EDC 103, i.e., the cathode chamber 212 and the anode chamber 211, generally operate to isolate the interior chambers of EDC 103, i.e., the depletion and concentration chambers 205,204, from the cathode 202 206 and anode 203 207. Generally, a sulfuric acid solution may be flowed between the

respective chambers 211,212, which operates to both maintain the respective electrodes (cathode and anode) clean, while also absorbing ions that may diffuse into the cathode chamber 212 and anode chamber 211. For example, the first membrane proximate the cathode is an anionic membrane 209, and therefore, when the electrical bias is applied to EDC 103, positive copper ions will not migrate from the adjacent concentration chamber through membrane 210 into the cathode chamber 212, so that copper will not deposit on the cathode 202 206. At the same time SO_4^{2-} ions will be carried away from the sulfuric acid solution into $\text{CuSO}_4/\text{H}_2\text{SO}_4$ concentrate. Similarly, the membrane positioned closest to the anode is an anionic membrane 209, and therefore, negative sulfate ions in the adjacent chamber will be urged to diffuse into the anode chamber 211 when the electrical bias is applied, compensating the loss of SO_4^{2-} taking place in the cathode chamber. Once these negative ions diffuse into the anode chamber 211, the they may be absorbed or slipped away by the sulfuric acid solution being flowed therethrough.

Please replace paragraph [0028] with the following amended paragraph:

[0028] Figure 4 illustrates another embodiment of an exemplary EDC 400 of the invention. EDC 400 is similarly constructed to EDC 103, in that EDC 400 includes a plurality of alternating anionic membranes 401 and cationic membranes 402 that cooperatively form alternating depletion chambers 408 and concentration chambers 409. In similar fashion to EDC 103, an inlet 410 is used to communicate used or spent electrolyte from a plating cell, such as a copper ECP cell, into the depletion chambers 408 of EDC 400. Immediately outward of the alternating sequence of depletion chambers 408 and concentration chambers 409 are individual isolation chambers 413. Isolation chambers 413 generally include a fluid inlet and a fluid outlet configured to receive and expel a circulating fluid, which may be a diluted sulfuric acid solution. In this configuration, the diluted sulfuric acid solution may be circulated between the respective isolation chambers 413 positioned on each side of EDC 400. Positioned outward of isolation chambers 413 are respective anode chamber 406 and cathode chamber 407. The anode chamber 406 and cathode chamber 407 are structurally

similar to isolation chambers 413, in that both anode chamber 406 and cathode chamber 407 include a fluid inlet and a fluid outlet configured to circulate a fluid solution between the respective anode and cathode chambers 406,407. However, EDC 400 is configured to circulate concentrated sulfuric acid between the respective anode chamber 406 and cathode chamber 407 via line 414.

Please replace paragraph [0029] with the following amended paragraph:

[0029] The membrane structure of EDC 400 is similar to the membrane structure of EDC 103. However, EDC 400 includes a slight variation on the membrane configuration in order to accommodate the additional isolation chambers 413. More particularly, the membrane structure still generally follows an alternating sequence, i.e., from left to right, an anionic membrane, then a cationic membrane, then an anionic membrane, etc. However, the membrane closest to the anode is generally a cation exchange membrane 403 414, such as, for example, a NAFION cation exchange membrane. The membrane closest to cathode 405 may be an anion cationic membrane 401 402.

Please replace paragraph [0030] with the following amended paragraph:

[0030] In operation, EDC 400 operates similarly to EDC 103 illustrated in Figure 2, as ~~the~~ the used electrolyte is supplied to depletion chambers 408 ~~V\$ via~~ via conduit ~~for~~ 10 410, while electrical bias is applied between cathode 405 and anode ~~for~~ 404 404. The application of the electrical bias causes positively charged ions in the used electrolyte solution to migrate towards the cathode 405, while negatively charged ions ~~or~~ are urged to migrate towards the anode 404. The configuration of cationic 402 and anionic 401 membranes operates to transport positive copper ions and negatively charged sulfate ions in concentration chambers between the respective membranes. The positive copper ions and the negative sulfate ions made ~~in~~ combine to form renewed concentrated copper sulfate, which may then be extracted from EDC 400 for reuse in a copper plating system. The remaining portions of the used electrolyte solution ~~flowed~~

flow through the depletion chambers 408 and may be extracted therefrom via conduit 412. The extracted solutions, which generally comprise diluted copper sulfate, sulfuric acid, in content material may be neutralized or disposed of. The isolation chambers 413 have a diluted sulfuric acid solution circulating between the two chambers, while the anionic chamber 406 and cationic chamber 407 have a concentrated sulfuric acid solution being circulated therethrough.

Please replace paragraph [0032] with the following amended paragraph:

[0032] Additionally, in similar fashion to EDC 103, EDC 400 and may include as few 3 or 4 chambers, and may include as many as 500 or more chambers, wherein chambers includes depletion chambers 408 and concentration chambers 409. Further still, the respective membranes in EDC 400 may also be configured to be very dense, i.e., several hundred membranes may be present in a 2 to 6 inch EDC housing. In the densely packed membrane configurations, EDC 400 may include an additional mesh that may be interstitially positioned between the respective anionic and cationic membranes. The additional mesh, which may be neutral with respect to its ionic ionic polarity, may essentially be used to space the respective anionic membranes slightly away from the cationic membranes, as contact between the respective membranes may hinder or destroy the polarity thereof. However, it is to be noted that the mesh separators are generally penetrable penetrable in either direction to both positive and negative ions, and therefore, will have little or no effect upon the ionic diffusion or flow within EDC 400.

Please replace paragraph [0035] with the following amended paragraph:

[0035] In operation, and EDC 500 may receive waste electrolyte, which generally includes positive copper and hydrogen ions, negative sulfate ions, and variously charged contaminated ions, in depletion chambers 501. The waste electrolyte flows through the depletion chambers 501, as indicated by the arrows illustrated in Figure 5. As the waste electrolyte flows through depletion chambers 501, the respective positive

and negative ions are drawn toward the cathode and anode according to their polarity, as described in previous embodiments. Therefore, as a result of the electrical potential applied across EDC 500 by the cathode 504 and anode 505, the output of depletion chambers 501 generally consists of primarily a diluted acid solution and traces of copper ions. The diluted acid solution is then returned to low concentration chambers 502 of EDC 500. The diluted acid solution travels through low concentration chambers 502 and is further separated by the electrical potential applied thereto, and therefore, the output of low concentration chambers 502 generally consists of a diluted solution containing positive copper ions, positive hydrogen ions and negative sulfate ions. High concentration chambers 503 does not receive a fluid inlet in a similar manner to depletion chambers 501 and low concentration chambers 502, however, high concentration chambers 503 have an output configured to dispense purified electrolyte solution in a concentrated form. The concentrated output of high concentration chambers 503 results from the diffusion of ions through the adjoining membranes into high concentration chambers 503, wherein the ions diffusing therein ~~their~~ in combined combine to form a concentrated copper sulfate solution and a concentrated sulfuric acid solution.

Please replace paragraph [0036] with the following amended paragraph:

[0036] In this embodiment, the presence of additional low concentration chambers fed by exhausted waste electrolyte has at least two advantages over conventional devices. First, embodiments of the invention decrease the back migration and diffusion of acid through membranes, as selectivity of membranes (a good anion membrane transports only anions, a bad one – 60% of anions and 40% -cations) increases when the membrane contacts with diluted solution. Therefore, so the low concentration chambers improve the efficiency of electrodialysis (amount of concentrate obtained) and increase the concentration of copper in concentrate chambers. Another advantage provided by embodiments of the present invention is that diluted sulfuric acid can be used to feed low concentration chambers as well, but cost of consumables decreases if one replaces the pure acid solution by exhausted waste electrolyte.